

# New insights on the high-pressure phase diagram of molecular CO<sub>2</sub>

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(Dated: February 6, 2008)

We report the discovery of a new molecular phase of carbon dioxide at high-pressure and high-temperature. Using x-ray diffraction, we identify this phase as the theoretically predicted high-temperature *Cmca* phase [Bonev *et al.*, Phys. Rev. Lett., **91**, 065501 (2003)]. Its relation with phase III, on one hand, and its relative stability with respect to phase IV, on the other hand, are discussed based on spectroscopic and melting data. The existence of this strictly molecular phase challenges the interpretation of phases IV and II as intermediate phases between the molecular and covalent-bonded forms of CO<sub>2</sub>.

In the last years, the intensive study of simple molecular systems (H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub> *etc.*) at very high pressures ( $P$ ) and temperatures ( $T$ ) have led to a wealth of remarkable discoveries, including new solid structures, insulator-metal transitions, symmetrization of H-bonds, polymerization or the formation of new covalent bonds. These findings have had important repercussions both on the fundamental level, since their understanding is usually challenging, and from a technological viewpoint, since they may open, for example, new routes for energy storage.

In this context, the discovery in 1999 by Iota *et al.* [1] of a non-molecular, quartz-like, phase of carbon dioxide by heating above 50 GPa has driven a large attention onto the behavior of this compound at elevated pressures. This phase was described as an extended network of four-fold coordinated carbon atoms, with a unusually large bulk modulus. Subsequently, new molecular phases were uncovered, named II and IV (Fig. 1) [2, 3]. From the large values of the C=O bond lengths found for these two phases, and the bent geometry of the molecule in phase IV, they were presented as precursors to the non-molecular phase. This interpretation, however, is not supported by a theoretical study by Bonev and co-authors [4] who found, first, that the equilibrium C=O bond length in any of the proposed structures is comparable to the free molecule value; and second, the stable structure in the domain of phase IV is not *Pbcn* with bent molecules, but a molecular *Cmca* structure with linear molecules.

This controversy enlightens a peculiarity of carbon dioxide compared to other simple molecular systems, that is, the presence of large metastabilities when going from one solid phase to the other. For example, the transition between phase I and III is a very sluggish one, spreading over 10 GPa at room temperature [2, 5, 6], and seem-

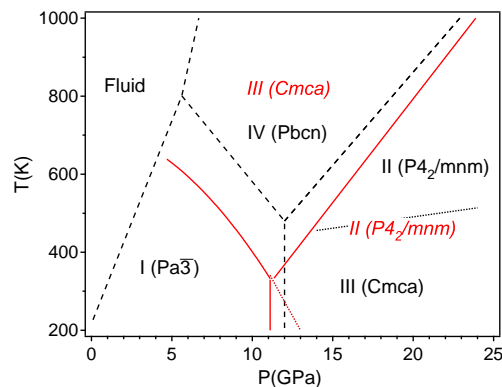


FIG. 1: (Color online) Experimental [2] (black dashed lines) and theoretical [4] (red solid lines) phase diagram of carbon dioxide. The theoretically predicted stable phases are indicated in italics, and the proposed experimental ones, in upright characters. The dotted lines are speculated kinetic lines.

ingly taking place through an intermediate structure [7]. These metastabilities make the task of determining the phase lines with accuracy a difficult one and more importantly, raise the question of which structure is actually the stable one at high P-T.

In this Letter, we report a new investigation of the phase diagram in the pressure region below 20 GPa and for temperatures up to 950 K. It reveals the presence of a previously unobserved phase (noted CO<sub>2</sub>-VII) above 640 K, intermediate between phases I and IV. Using x-ray diffraction, we determine the structure of this phase and show that it is the theoretically predicted high P-T *Cmca* phase. The distinction between CO<sub>2</sub>-VII and CO<sub>2</sub>-III is revealed by comparing their Raman spectrum. We also report measurements of the melting lines of this new phase and phase IV which allow us to determine their relative stability. Finally we show that the discovery of this phase has important consequences on the nature of phases IV and II.

The experiments reported here were done in resistively heated diamond anvil cells. The techniques are identical to the ones presented in details in Ref. 8.

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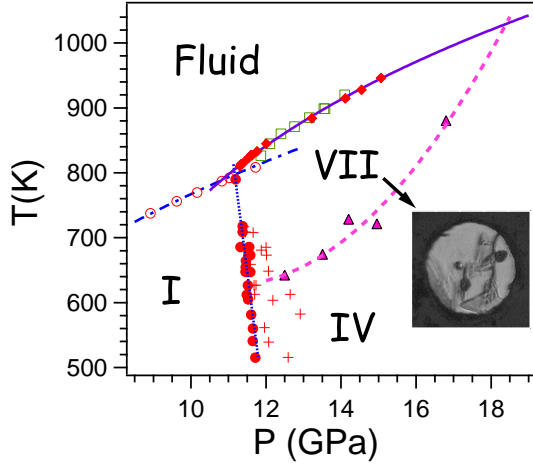


FIG. 2: (Color online) Presently determined phase transition points. The melting curve of phase I reported in Ref. 8 is shown as the dot-dashed line;  $\circ$ : melting points of phase I (present work);  $+$  and  $\bullet$ : I-IV transition measured respectively on loading and unloading;  $\blacktriangle$ : VII to IV transition;  $\square$ : melting points of phase VII;  $\blacklozenge$ : melting points of phase IV. The experimental uncertainties on  $P$  and  $T$  are within the symbol sizes. The curves are fit to the data. The melting points of phase IV and VII are well fitted by the Simon-Glatzel law [9]:  $T = T_0[1 + (P - P_0)/a]^{1/c}$  with  $T_0 = 805$  K,  $P_0 = 11.15$  GPa,  $a = 46(8)$  GPa and  $c = 3.8(6)$ . The photograph shows the sample of phase VII (with pressure sensors) viewed through the diamond anvils at 770 K and 11.8 GPa.

We first investigated the I-IV transition line between 500 and 790 K by visual observation and Raman spectroscopy, tuning the pressure around the transition in order to observe it both on loading and unloading. As Fig. 2 shows, the unloading transition points lie on a well defined nearly vertical line, whereas the loading ones are quite scattered. This hysteresis decreases with temperature and nearly disappears above 700 K. From the unloading line and the previously reported melting curve [8], we localize the I-IV-Fluid triple point at 800(5) K and 11.2(1) GPa.

For  $T > 640$  K and  $P > 12$  GPa, compression of phase I systematically produced a new phase, noted hereafter CO<sub>2</sub>-VII, which in turn transformed to phase IV by further compression. CO<sub>2</sub>-VII was easily identifiable both visually and from its Raman spectrum. The transition was usually sharp and the new phase visibly birefringent (Fig. 2). Fig. 3 reports the Raman spectra collected along an isotherm at 719 K, following the transition from phase I to IV through phase VII. The characteristics of the Raman spectrum of CO<sub>2</sub>-VII will be analyzed below. At 640 K the I-VII and VII-IV transitions took place at 12.3 GPa and 12.55 GPa respectively. Increasing the temperature, the pressure domain in which phase VII is observed grows larger: at 726 K the two transitions were localized at 12.1 and 14.2 GPa respectively. Decompression of phase VII at 705 K led to phase I at 11.8 GPa,

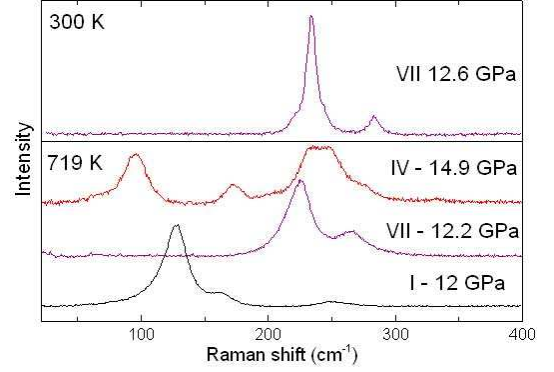


FIG. 3: (Color online) Raman spectra collected on quenched phase VII at 300 K (top) and along an isotherm at 719 K going from phase I to IV through VII (bottom).

i.e. slightly above the IV to I transition pressure (11.4 GPa).

To investigate the structure of phase VII, we collected x-ray diffraction spectra following an isotherm at 726 K, using the monochromatic ( $\lambda = 0.3738$  Å) angular dispersive setup on beamline ID27 of the European Synchrotron Radiation Facility in Grenoble. The images were collected during rotation of the cell around the  $\omega$  axis. The observed  $d$ -spacings match very well an orthorhombic unit cell with 4 molecules and the following lattice parameters at 12.1 GPa, 726 K:  $a = 4.313(1)$  Å,  $b = 4.746(1)$  Å,  $c = 5.948(1)$  Å. All the peaks could be indexed by considering three distinct diffracting crystallites rotated around the  $c$  axis with respect to each other. Visible peaks obey the following conditions:  $hkl$ :  $h+k = 2n$ ;  $hk0$ :  $h, k = 2n$ ;  $0kl$ :  $k, l = 2n$ , from which we deduce the space group  $Ccmb$ . This is the same group as  $Cmca$  but with a different choice of axes, i.e. with  $a$  and  $b$  axes inverted.

The existence of a  $Cmca$  polymorph in high-pressure CO<sub>2</sub> was first predicted by Kuchta and Etters using lattice dynamics calculations [10]. In their structure, the axes are in the order  $a < b < c$  and the molecules lie on the  $(bc)$  plane, tilted by  $\varphi = 52^\circ$  with respect to the  $c$  axis. More recent calculations based on density functional theory (DFT) [4, 12] found that the optimized  $Cmca$  structure, stable at high  $P - T$ , was such that  $a > b$  and  $\varphi = 54^\circ$ . Since we find the same axis order, we used this structure as a starting point for refinement. The latter was done against the measured intensities of 16 independent reflections originating from the same crystallite [16]. Convergence was obtained down to an  $R$ -factor of 0.069, yielding for atomic positions,  $C$  on (0,0,0) and  $O$  on [0,0.212(3),0.109(1)], with isotropic temperature factors  $U$  of 0.0637 Å<sup>2</sup> ( $C$ ) and 0.0314 Å<sup>2</sup> ( $O$ ). The refined structure, shown on Fig. 4, presents a  $\varphi$  angle of 54.5(1) $^\circ$ , in excellent agreement with the DFT calculations [4, 12]. The C=O bond length is 1.13(1) Å,

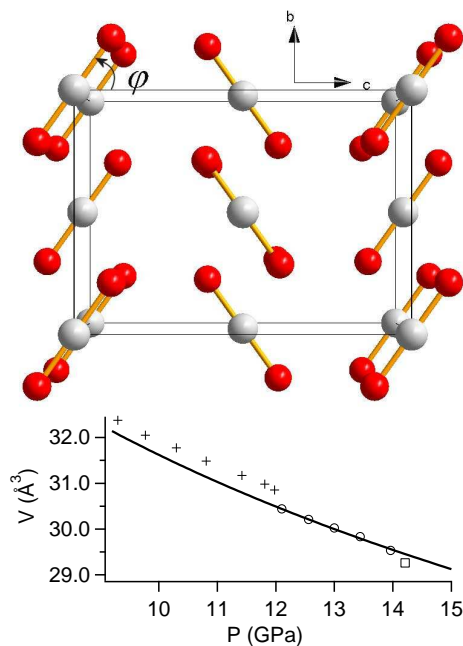


FIG. 4: (Color online) Structure of the  $Cmca$  phase VII at 726 K and 12.1 GPa, projected along the  $a$  axis. The molecules lie on the  $(bc)$  plane, tilted by  $\varphi = 54.5^\circ$  with respect to the  $c$  axis; in the bottom, the volume per molecule vs. pressure is shown along the isotherm at 726 K for phase I (+), VII (○) and IV (□). The solid line is the theoretically computed equation of state for the  $Cmca$  phase at 0 K [4]. The volume discontinuity is 1.2% between phase I and VII and 0.66% between phase VII and IV.

i.e. slightly shorter than the one found [13] for phase I at 1 GPa [1.1486(9) Å], and again in good agreement with calculations. We can thus conclude that phase VII is the  $Cmca$  phase predicted by Bonev *et al.* [4] to be stable in this  $P-T$  range. This is further corroborated by the excellent agreement observed between the presently determined and calculated equation of state [4] (Fig. 4, bottom).

It is worth pointing out that the  $Cmca$  space group is also the one designated for the room-temperature high-pressure phase III. The structure of this phase was identified by Aoki *et al.* [11], and later by Yoo *et al.* [5], as the one predicted by Kuchta and Etters [10]. However we note that collecting good diffraction data on phase III has been so far challenging due to the highly strained nature of this phase. As a result, its structure is still not well constrained. In their work, Bonev *et al.* [4], like previous authors, assimilated the theoretical  $Cmca$  phase with phase III, only relocating its stability domain to that of phase IV (Fig. 1) (the  $Cmca$  structure was found unstable at 300 K, so phase III was presented as metastable at this temperature). This raises the question of whether phase VII is identical to phase III. First of all, we note that the experimental existence domains of the two phases are not connected in the  $P-T$  space: phase

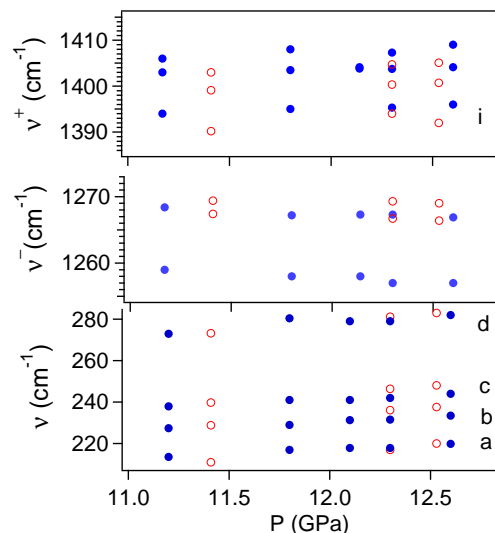


FIG. 5: (Color online) Room temperature pressure evolution of external and internal modes in phase VII (●) and III (○). The mode i comes from the  $\approx 1\%$  of  $^{13}\text{C}^{16}\text{O}_2$  molecules.

III transits to II at  $\approx 450$  K whereas  $\text{CO}_2$ -VII is only observed above 640 K. To go further, we have compared their Raman spectra collected during decompression at 300 K. Phase VII could be quenched to room temperature, which is a common property of all the high  $P-T$  phases of carbon dioxide. Phase III was produced by compression of phase I at 300 K and annealed to 440 K to release the stress. The pressure evolution of the Raman modes is shown in Fig. 5. The four lattice phonon modes and two components of  $\nu^+$  and  $\nu^-$  [17], observed in both cases, match group theory predictions for the  $Cmca$  structure. A  $\approx 5 \text{ cm}^{-1}$  frequency difference between the two solids is registered in the central lattice modes (b and c in the figure) and in the  $\nu^+$  region, whereas the difference increases up to  $10 \text{ cm}^{-1}$  for the components of  $\nu^-$ . This indicates that the two structures are indeed different. Further work is however needed to clarify this question.

By contrast with the theoretical phase diagram in Fig. 1, the  $Cmca$  phase is not the only one present at high temperatures, since it transits to phase IV at higher pressure. As a matter of fact, we could only obtain phase VII by compression of phase I and never by heating or decompressing phase IV. This is reminiscent of the fact that phase III has itself only been obtained from compression of phase I. Since this was taken as an indication of the metastable character of phase III, this raises the question of which of phase VII or IV is the stable structure beyond the I-(IV,VII) transition line.

To answer this, we have measured the melting curve of  $\text{CO}_2$  for  $T > 800$  K, extending the determination presented in Ref. 8. A melting point was defined as the  $P-T$  conditions where the solid/fluid equilibrium was visually observed and the solid phase was identified by its Raman

spectrum. Melting of solid I was followed up to 808 K and 11.7 GPa. At 810 K and 11.8 GPa the sample suddenly transited into pure phase VII. It was then decompressed in order to melt it and heated to 827 K. Increasing the load at this temperature produced the equilibrium between solid VII and fluid at 12.1 GPa. We then followed the melting curve of phase VII up to 920 K. Compression of phase VII at 879 K produced phase IV at 16.8 GPa. Surprisingly, the latter could be decompressed down to the equilibrium between phase IV and the fluid, at 884 K and 13.2 GPa. We then measured several melting points of phase IV from 810 K to 946 K. As shows Fig. 2, this melting curve is not distinguishable from the one of phase VII within our experimental uncertainties ( $\pm 0.2$  GPa and  $\pm 5$  K at these  $P - T$  conditions).

The fact that the solid phase obtained from the melt above 827 K is phase VII confirms that it is indeed the stable phase at these temperatures and pressures. However, the closeness of the melting curves shows that the energy difference between phase IV and VII is very small, since at melting the Gibbs free energy of the fluid and solid phases are equal. The fact that we could decompress phase IV down to the solid/fluid equilibrium without reverting to phase VII gives an indication that there is a strong potential barrier hindering this transformation. This also explains why we were able to measure the transition line between phase I and IV by compression of phase I even in the temperature range where we observed phase VII: since we tuned the pressure closely around the transition, it is likely that part of the sample was still in phase IV, forcing the transition from phase I to IV without passing via phase VII.

Fig. 4 shows that the VII-IV transition is accompanied by a small volume decrease (0.66% at 726 K). Since the slope of the transition line is positive, the Clapeyron's law imply that phase VII has a larger entropy (by about 4 J/mole) than phase IV. This agrees with the calculation of Bonev *et al.* [4] who found that the *Cmca* structure is stabilized at high temperatures by its larger entropy due to the contribution of a soft acoustic phonon. Extrapolating the measured melting line and VII-IV transition line gives a possible IV-VII-F triple point at  $\approx 1030$  K and 18.4 GPa.

Phase VII is thus the stable solid phase beyond phase I for  $T > 640$  K but phase IV becomes more stable at higher pressures. This suggests that the structure of phase IV needs to be revised, since the proposed *Pbcn* structure [14] was found by Bonev *et al.* [4] to be thermodynamically unstable with respect to the *Cmca* structure in the whole  $P - T$  field of phase IV.

Finally, our findings are useful in clarifying the present debate on the molecular character of the high  $P$ - $T$  phases IV and II of carbon dioxide. As mentioned in the beginning, the C=O bond lengths found experimentally for these two phases [14, 15] are much larger than in phase I [13], which was taken as evidence that these phases

are intermediate forms between the molecular and covalent bonded solids. Bonev *et al.* [4] found that the bond lengths in either of phase II or IV structure shortened to a value comparable to the one in phase I; the calculated energy difference between the long and short bond lengths is in excess of 3 and 6 eV per molecule respectively in phase II and IV. We have shown here that phase VII is a strictly molecular phase, with a C=O bond length close to that of phase I at 1 GPa. Moreover, from the volume and entropy jumps at the VII-IV transition, we estimate an internal energy difference of about 13 meV per molecule between the two phases at 726 K: this strongly suggests that phase IV, and most likely phase II [18], are strictly molecular phases too, in agreement with a recent spectroscopic study [6].

We thank B. Canny (IMPMC) and M. Mezouar (ESRF ID27) for their help with the experiments.

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  - [17]  $\nu^+$  and  $\nu^-$  come from the Fermi resonance between the overtone of the bending  $2\nu_2$  and the symmetric stretching mode  $\nu_1$ .
  - [18] Ref. 4 reports a calculated energy difference of 20.6 meV/molecule between the molecular *Cmca* and *P4<sub>2</sub>/mnm* (phase II) structures.